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TENSILE PROPERTIES OF
PALLADIUM-SILVER ALLOYS
WITH ABSORBED HYDROGEN

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16. Abstract The alloys 90Pd-10Ag, 80Pd-20Ag, 70Pd-30Ag, 60Pd-40Ag, and 50Pd-50Ag containing absorbed hydrogen were tested in tension. The results show the tensile properties to be independent of the $\alpha - \beta$ phase transition. Also, hydrogen in the lattice does not necessarily cause embrittlement or poor elongation. The changes in the tensile properties appear dependent on the electron to atom site ratio.					
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TENSILE PROPERTIES OF PALLADIUM-SILVER ALLOYS

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SUMMARY

The tensile properties of the alloys 90Pd-10Ag, 80Pd-20Ag, 70Pd-30Ag, 60Pd-40Ag, and 50Pd-50Ag were studied as functions of hydrogen content. The results indicate the changes in characteristics of these properties are independent of the $\alpha \rightarrow \beta$ phase transitions. Rather, the changes in the tensile properties seem dependent on the electron to atom site ratio. Also, the hydrogen in the lattice does not necessarily cause embrittlement or poor elongation.

INTRODUCTION

Smith and Otterson (ref. 1) report that plots of yield strength (YS), ultimate tensile strength (UTS), and percent elongation against hydrogen-palladium atom ratio (H/Pd) show abrupt changes near $H/Pd \simeq 0.02$ and again near 0.5. The palladium-hydrogen (Pd-H) system has two distinct face centered cubic (fcc) phases at 293 K. The α -phase, with an upper limit of its lattice parameter of 0.3895 nanometer, exists below $H/Pd \simeq 0.02$. The β -phase, with a lattice parameter of 0.4025 nanometer, exists for $H/Pd > 0.6$. Both phases coexist for $0.02 < H/Pd < 0.6$. In the α -phase region, the YS, UTS, and percent elongation increase strongly with increasing H/Pd for both annealed and unannealed palladium (Pd). In the two-phase region these properties decrease with increasing H/Pd except for YS of annealed palladium. The YS of annealed palladium continues to increase in the two-phase region but with a smaller slope. In the pure β -phase region, these properties remain essentially constant with increasing H/Pd.

Aside from the obvious difference in lattice parameter, the major difference between α Pd and β Pd is their electron characteristics. The 4d-band of α Pd is

unfilled containing initially 0.36 hole (ref. 2) whereas the 4d-band of β Pd is thought to be filled (ref. 3). Smith and Otterson (ref. 1) suggest that these changes in the electron distribution, independent of any crystallographic change, are a major factor contributing to the observed tensile behavior. However, one might argue from the Pd-H data of (ref. 1) that the change in tensile properties is due to the initiation of a crystallographic change (appearance of the β -phase) near H/Pd $H/Pd \approx 0.02$. One objective of this work is to help determine which of these ideas is correct by alloying silver (Ag) into the host palladium lattice.

Silver is completely soluble in palladium with no observable superstructure at least to the 50Pd-50Ag composition (refs. 3 and 4). When palladium is alloyed with silver the lattice constant of the alloy increases with increasing silver content as shown in figure 1. In the palladium-silver-hydrogen (Pd-Ag-H) system, the upper limit of the lattice parameter of the α -phase increases and the lower limit of the lattice parameter of the β -phase decreases as the silver content in the alloy increases (ref. 5, p. 144, fig. 9.4). In fact, for silver contents of 30 atomic percent or more in the palladium-silver (Pd-Ag) alloy, no second metallic phase is formed for any H/Pd value at 293 K. And the lattice remains fcc with no discontinuities in the lattice expansion as hydrogen is absorbed. Also, as palladium is alloyed with silver, the effective number of palladium 4d-holes decreases. This alters the 4d filling by the absorbed hydrogen.

Investigation of the Pd-Ag-H system may also yield additional information on the brittleness or poor elongation found in the pure β -phase of the Pd-H system. Smith and Otterson (ref. 1) suggest that the brittleness in β Pd is not necessarily due to the presence of the interstitial hydrogen, but rather is caused by the severe strain hardening of the palladium lattice that occurs during the formation of β Pd. (Palladium wires remained brittle after desorption of hydrogen from β Pd.).

The alloying of palladium with silver permits us to vary the amount of lattice strain induced in the host lattice due to hydrogen absorption. With this approach, the variation of electronic structure on the tensile properties may be better understood. Tensile tests were performed only on annealed Pd-Ag wires with H/Pd values varying from zero to the neighborhood of 0.6. The results are interpreted primarily in terms of the electronic structure and crystallographic transition.

EXPERIMENTAL

The Pd-Ag alloys used in this work were in wire form of approximately 0.254 millimeter diameter and between 5.3 and 7.6 centimeters in length. The atomic percent compositions of the wires were nominally 90Pd-10Ag, 80Pd-20Ag, 70Pd-30Ag, 60Pd-40Ag, and 50Pd-50Ag. The compositions as determined by an independent company are shown in table I. Spectrographic analysis for impurities was done at NASA Lewis Research Center and is shown in table II. The wires were annealed at 1023 K for 2 hours in a vacuum of approximately 8×10^{-7} N/m² (6×10^{-9} torr). The wires were charged with hydrogen electrolytically in a 0.1 N H₂SO₄+Na₂S solution. The charging times varied from a few seconds to approximately 2 hours depending on the H/Pd value desired. The time between removal of the specimens from the charging solution and the start of the tensile test was approximately 10 minutes.

For the tensile tests, the gage lengths were approximately 1.27 centimeters. The cross head speed was 50.8 micrometers per minute for a strain rate of 4×10^{-3} per minute. The specimens were held in hydraulically operated grips with a force of 3.45×10^4 newton per square meter (50 lb/in.²). The elongations were determined to be correct to within 15 percent. The YS and UTS were calculated using the initial cross sections. The YS is based on 0.2 percent permanent extension.

After the tensile tests, the wires were placed in liquid nitrogen to prevent hydrogen loss until they could be weighed and placed in the desorption chamber of the mass spectrometer. The time lapse between removal of the wires from liquid nitrogen and placing them in the desorption chamber did not exceed 10 minutes. The hydrogen was desorbed at 870 K. A hydrogen determination was made with an accuracy of 1 percent for both sections of the wire adjacent to the fracture.

RESULTS

The YS and UTS plotted against silver content in palladium are shown in figure 2. Both YS and UTS show maximum values near 30 atomic percent silver. In figure 3, the percent elongation plotted against atomic percent silver in palladium shows a maximum value between 30 and 40 atomic percent silver. In both figures 2 and 3, the lowest values are for pure palladium. Figure 4 shows YS and UTS plotted against H/Pd for palladium, 90Pd-10Ag, 80Pd-20Ag, 70Pd-30Ag, 60Pd-40Ag, and 50Pd-50Ag, respectively. (Fig. 4(a) shows the results in which palladium was

annealed and unannealed prior to hydrogen absorption (ref. 1)). A maximum in both YS and UTS seems to occur near $H/Pd \approx 0.02$. The limited number of data points is due to the small number of available specimens.

Figure 5 (from ref. 1) shows percent elongation plotted against H/Pd for palladium (annealed and unannealed) and 90Pd-10Ag, 80Pd-20Ag, 70Pd-30Ag, 60Pd-40Ag, and 50Pd-50Ag. In all plots, H/Pd values near 0.02 yielded the largest percent elongation. The percent elongation values decrease as the values for H/Pd exceed 0.02. The percent elongation dropped to 4.5 percent for the 90Pd-10Ag alloy with an H/Pd value near 0.55. This result is similar to that for Pd-H where only the β -phase is present (fig. 5(a) and $H/Pd > 0.55$; see ref. 1).

These results seem to indicate that the maximums in the tensile properties occur near $H/Pd = 0.02$ whether or not the β -phase is present.

DISCUSSION

We now propose a qualitative description of the influence of hydrogen on the yield and ultimate tensile strengths for Pd-Ag alloys. The description is based on the variation of electron occupation of the 5sp and 4d-bands and strain hardening of the lattice. The binding or cohesive energy of a metal may be increased if electrons in the upper filled regions are either removed or placed in lower levels (ref. 6, p. 428). This argument is used to explain why the transition metals nickel (Ni), palladium, and platinum (Pt) have higher cohesive energies than their neighbor nontransition metals copper (Cu), silver, and gold (Au) (ref. 6, pp. 427-428 and ref. 7, pp. 56-60).

From photoemission studies of the energy levels in the Pd-H system, Eastman, Cashion, and Switendick describe the changes in the electron state distribution of palladium caused by hydrogen absorption (ref. 2). Their results show the formation of "new" states centered about 1.5 eV below the bottom of the palladium 4d-band. These "new" states are hybridized bonding states which derive from the strong interactions of the hydrogen 1s electron with already occupied low-lying palladium states. We suggest these "new" states lower the center of gravity of the 4d-band thereby increasing the cohesive energy (as discussed in ref. 6, p. 428). This helps account for the increase in the strength of palladium for $0 < H/Pd \lesssim 0.02$ as shown in figure 4(a). (This increase due to hydrogen absorption is independent of the ini-

tial state of the palladium (annealed or unannealed)). As hydrogen absorption continues, hydrogen-hydrogen (H-H) interactions start to occur and pull down previously unoccupied 5sp-states below the top of the 4d-band which permits the 4d-band to fill at $H/Pd \approx 0.6$ instead of 0.36. These filled states first start to appear near $H/Pd \approx 0.02$ for palladium. At $H/Pd \approx 0.6$, all the 4d-states are filled and the bulk palladium appears as a nontransition metal. The argument from Seitz (ref. 6) suggest that the cohesive energy should be lower when the d-band is filled. In figure 4(a), the rule of mixtures may be applied for $0.02 < H/Pd < 0.6$ where we find the transition metal palladium (unfilled 4d-states) coexisting with nontransition metal palladium (filled 4d-states).

We assume the foregoing discussion to be a special case of the Pd-Ag-H system in which the atomic percent silver is zero. When the silver content is between 0.0 and 50 atomic percent of the Pd-Ag alloy, the effect of varying the number of 4d-electrons on the tensile properties is first seen in figure 2 with $H/Pd = 0$. The plots of YS and UTS against atomic percent silver in palladium show maximums near 30 atomic percent silver instead of 50Pd-50Ag as is the case for the gold-silver (Au-Ag) system (ref. 8) (see insert fig. 2). This continued increase in YS and UTS as the silver content decreases below 50 atomic percent silver may be due to the appearance of holes in the 4d-band. This would cause an increase in the cohesive energy. Since the silver atom contributes part of its 5s-electron to the palladium 4d-band (ref. 9), the H/Pd value for filling the palladium 4d-band should decrease with increasing silver content and go to zero at a silver concentration of >50 atomic percent. Also, the presence of silver may decrease the H-Pd interaction (ref. 9) thereby reducing the enhancement of YS and UTS with increasing H/Pd . Additional data may better define the maximum values of YS and UTS and identify the hydrogen concentration for these maximums more precisely.

The maximums for the tensile properties plotted against H/Pd tend to occur near $H/Pd \approx 0.02$ for the Pd-Ag-H system including 0 atomic percent silver. For Pd-H, the appearance of the β -phase (or discontinuity in the lattice expansion) also occurs near $H/Pd \approx 0.02$. We suggest this expansion is to accommodate the proximity of hydrogen ions for H-H interactions. This is also the region where an inflection in the plot of electrical resistivity against H/Pd is found (ref. 5, p. 11; ref. 10), fig. 4), and where we assume the first filled 4d-states start to appear. As silver is added to palladium, the lattice expands linearly and permits some H-H interac-

tions to occur without precipitating the β -phase. And the β -phase (discontinuity in the lattice expansion) starts to appear at higher H/Pd values. As previously stated, for silver contents in excess of 30 atomic percent of the Pd-Ag alloy, no lattice discontinuity is found in the Pd-Ag-H system. We therefore conclude that the maximums in the tensile properties near $H/Pd \approx 0.02$ are independent of a lattice discontinuity or appearance of the β -phase.

The results of YS and UTS plotted against H/Pd for the 90-Pd-10Ag alloy (fig. 4(b)) appear similar to those of the Pd-H system in which the palladium was annealed prior to hydrogen absorption (fig. 4(a)). For both metals, the strength for $H/Pd \approx 0.5$ is greater than for $H/Pd = 0$. The most dramatic difference occurs in comparing the yield strengths. The continued increase in the YS of palladium for $H/Pd > 0.02$ is accounted for by strain hardening during formation of the β -phase (ref. 1). This also accounts for the differences in UTS.

However, for the remaining alloys, the YS and UTS values for $H/Pd \approx 0$ are higher than their respective values for $H/Pd \approx 0.3$ to 0.6 . This is to be expected since the strength of a metal with a filled d-band ($H/Pd \approx 0.3$ to 0.6) should be weaker than the same metal with an unfilled d-band ($H/Pd \approx 0$). A decrease in the strain hardening effect permits the change in the electron distribution effect, occurring between the 5sp- and 4d-bands, to be more easily observed. Figure 6 shows the difference in lattice parameter between β_{\min} and α_{\max} (Δa_0) decreases as the silver content increases (also found in ref. 5). We assume that this decrease in Δa_0 will result in a decrease in strain hardening. The Δa_0 for 80Pd-20Ag-H is small enough that the strain hardening effect does not obscure the effect of the change in electron distribution between the 5sp- and 4d-bands. In the alloys 70Pd-30Ag-H, 60Pd-40Ag-H, and 50Pd-50Ag-H, the strain hardening is apparently minimal or nonexistent and the expansion due to hydrogen is primarily elastic. No second phase exists for these alloys.

When we consider the elongations with respect to strain hardening due to hydrogen absorption, the lowest values of percent elongation occur in Pd-H and 90Pd-10Ag-H with H/Pd values near 0.6. [Both metals are considered to be highly strained or work hardened for $H/Pd \approx 0.6$.] However, for the remaining alloys, the strain hardening for $H/Pd \approx 0.3$ to 0.6 is assumed to be low or zero and the resultant percent elongations are of the order of the percent elongations of the alloys prior to hydrogen absorption. In studying the details of the elongations, especially

in the neighborhood of $H/Pd \simeq 0.02$, it may be of value to investigate electrical binding and stacking fault energies. These aspects of work are closely related to electron distribution about the metallic atoms (ref. 11, pp. 179-180; ref. 12, pp. 71,72).

CONCLUSIONS

Tensile tests were conducted on alloys of palladium-silver-hydrogen to gain additional understanding of the changes in the mechanical properties of 2 metallic systems due to hydrogen absorption. The palladium-silver alloys were nominally 90Pd-10Ag, 80Pd-10Ag, 70Pd-30Ag, 60Pd-40Ag, and 50Pd-50Ag with the H/Pd values varying from 0.00 to approximately 0.6. In this work we were able to vary the electron distribution between the 5sp- and 4d-bands. Also, we could either vary the H/Pd values at which crystallographic changes would occur or prevent them from occurring depending upon the silver content in the alloy. The following conclusions were reached:

1. This work tends to support the idea that changes in the electron distribution should be considered when studying the tensile properties of the palladium-hydrogen (Pd-H) and palladium-silver-hydrogen (Pd-Ag-H) systems. The appearance of the β -phase proved to be unrelated to any of the observed tensile properties. While we associate the β -phase with filled 4d-states, filled 4d-states can obviously exist without the presence of the β -phase. Additional support for considering changes in the electron distribution comes from the YS and UTS values of the Pd-Ag-H alloys with filled 4d-bands dropping below the prehydrogen absorption values. (The presence of silver decreases the strain hardening component of hydrogen absorption.).

2. In this system, it has been shown that the presence of hydrogen does not necessarily cause brittleness or poor elongation. Moreover, if strain hardening is reduced by decreased lattice expansion during hydrogen absorption, then no adverse changes in ductility occur.

3. The phase mixture rule can be applied when both transition metal and non-transition metal are present at the Pd-H or Pd-Ag-H systems.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, May 5, 1975,
506-16.

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TABLE I. - ANALYSIS OF SILVER
IN PALLADIUM-SILVER ALLOYS

Alloy designation	Silver content, atomic percent ^a
90Pd-10Ag	9.79, 9.60
80Pd-20Ag	20.02, 19.81
70Pd-30Ag	26.81, 29.00
60Pd-40Ag	38.22, 38.99
50Pd-50Ag	50.72, 50.05

^aResults are from two samples
of each alloy.

TABLE II. - SPECTROGRAPHIC ANALYSIS OF IMPURITIES IN PPM IN
PALLADIUM-SILVER ALLOYS

Nominal atomic percent of Pd and Ag	Al	Co	Cr	Cu	Fe	Ni	Rh	Si	Ti	Total impurities
Pd	50	<1	3	3	70	50	---	25	75	<277
90Pd-10Ag	30	10	35	70	220	100	250	40	120	875
80Pd-20Ag	50	10	55	75	220	190	330	240	40	1210
70Pd-30Ag	90	<10	400	80	300	100	100	190	<50	<1320
60Pd-40Ag	180	2	85	60	200	60	130	500	60	1277
50Pd-50Ag	70	<10	60	80	100	<50	200	<50	<50	<670

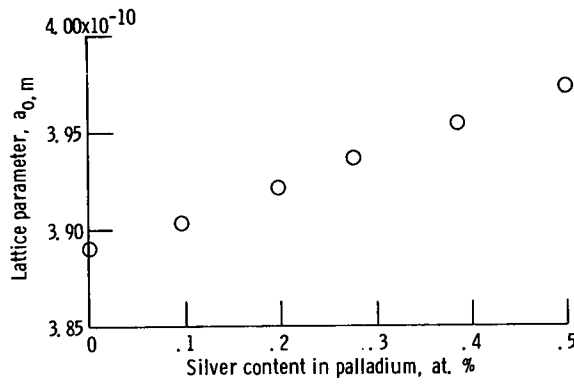


Figure 1. - Lattice parameter as function of increasing silver content in palladium.

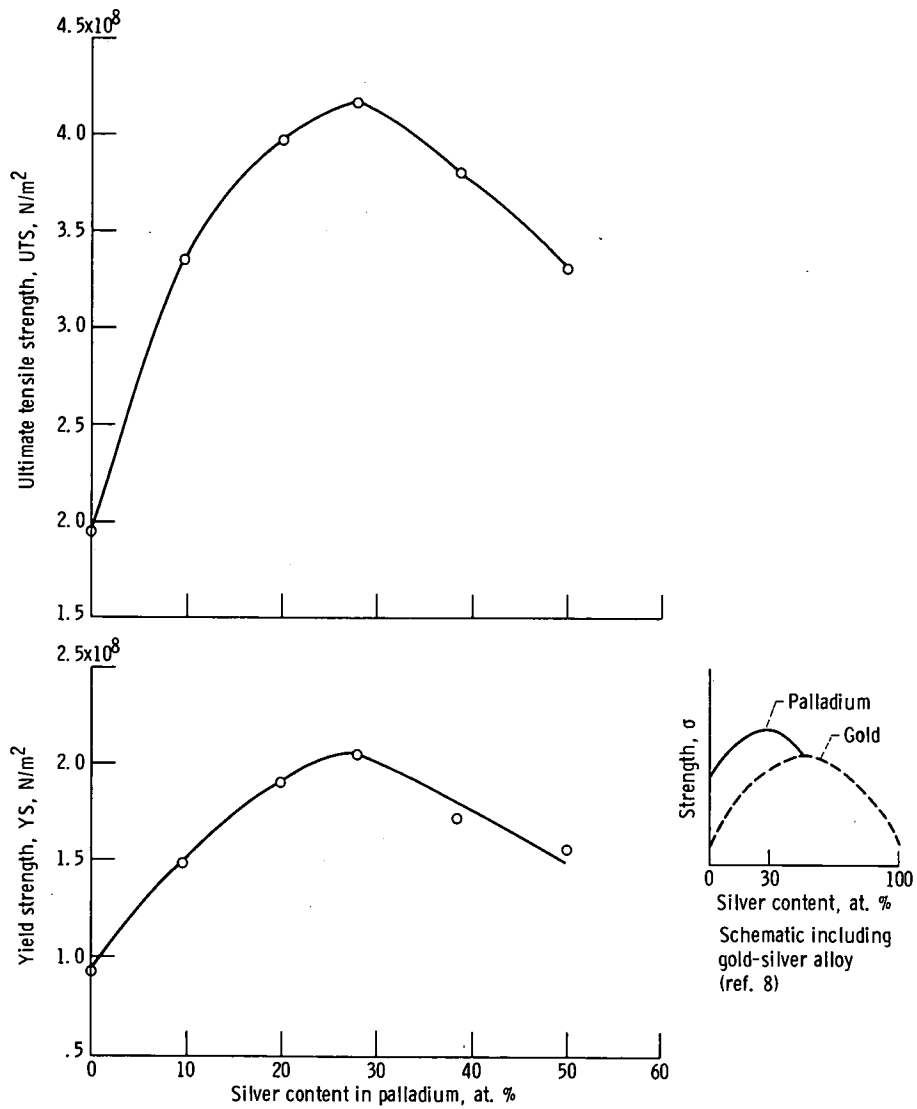


Figure 2. - Ultimate tensile and yield strengths plotted against silver content.

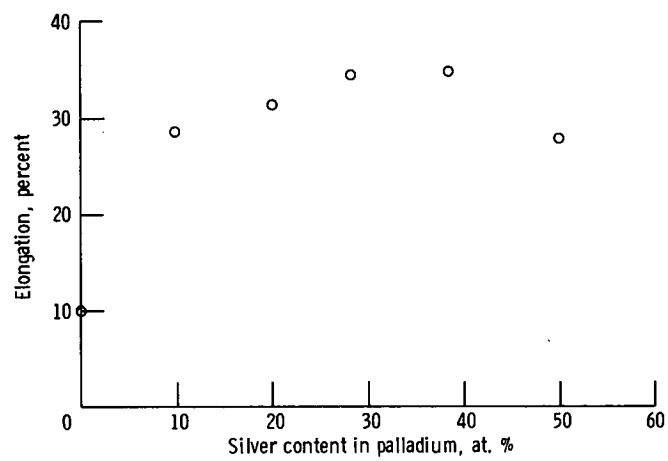


Figure 3. - Percent elongation plotted against silver content in palladium.

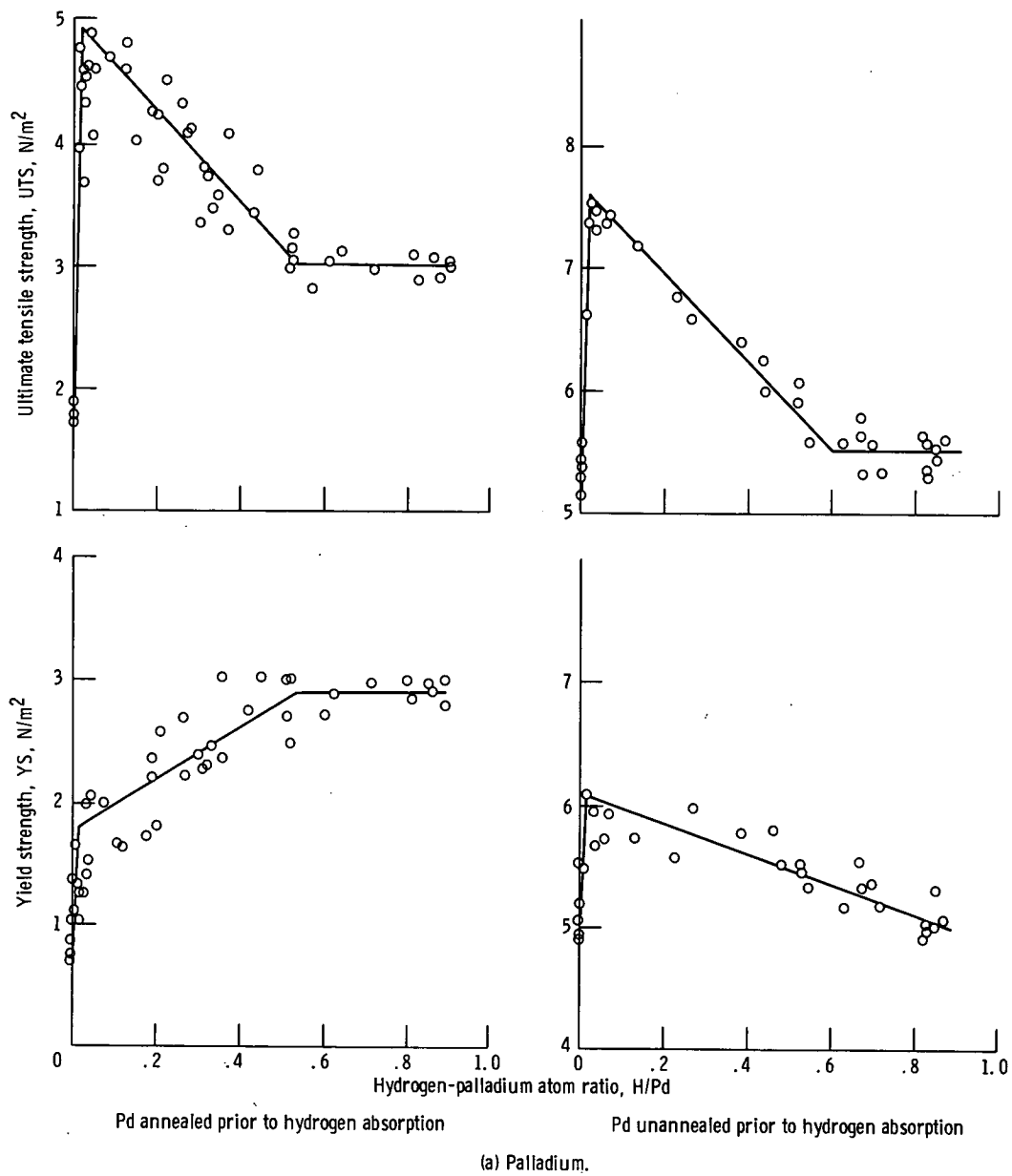
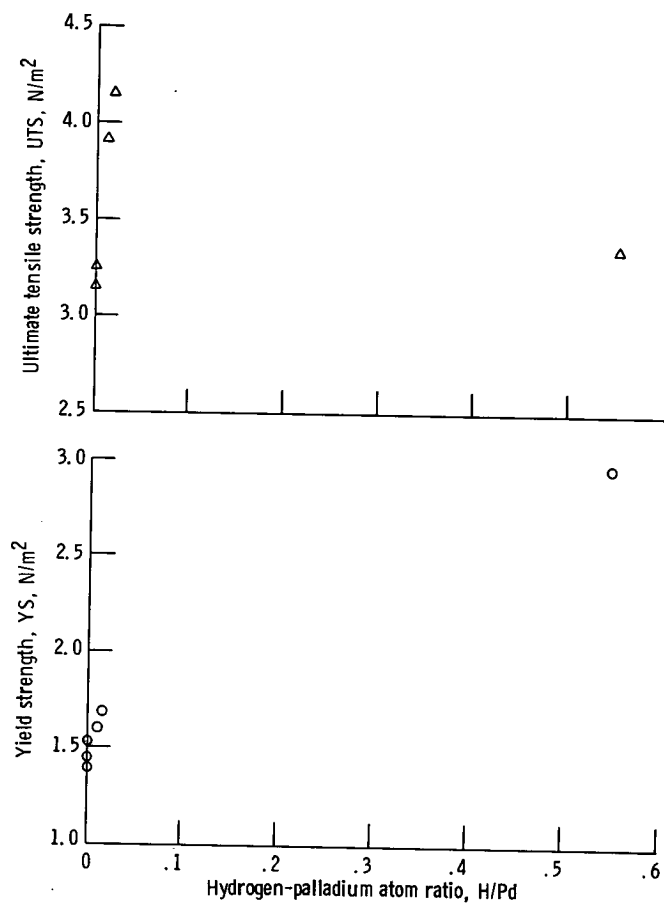
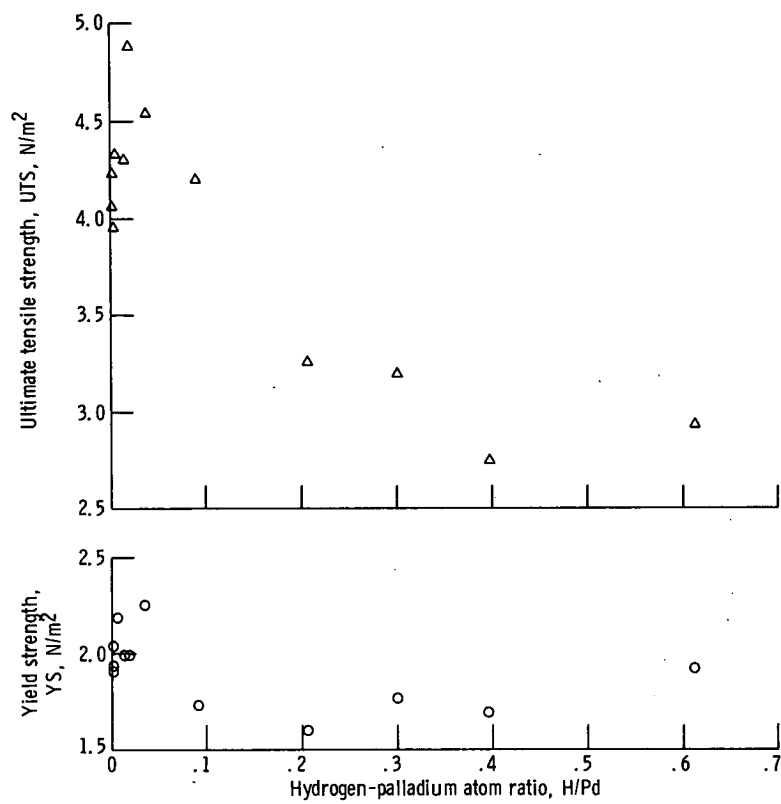


Figure 4. - Ultimate tensile and yield strengths plotted against hydrogen content in palladium (Pd), 90Pd-10Ag, 80Pd-20Ag, 70Pd-30Ag, 60Pd-40Ag, 50Pd-50Ag.



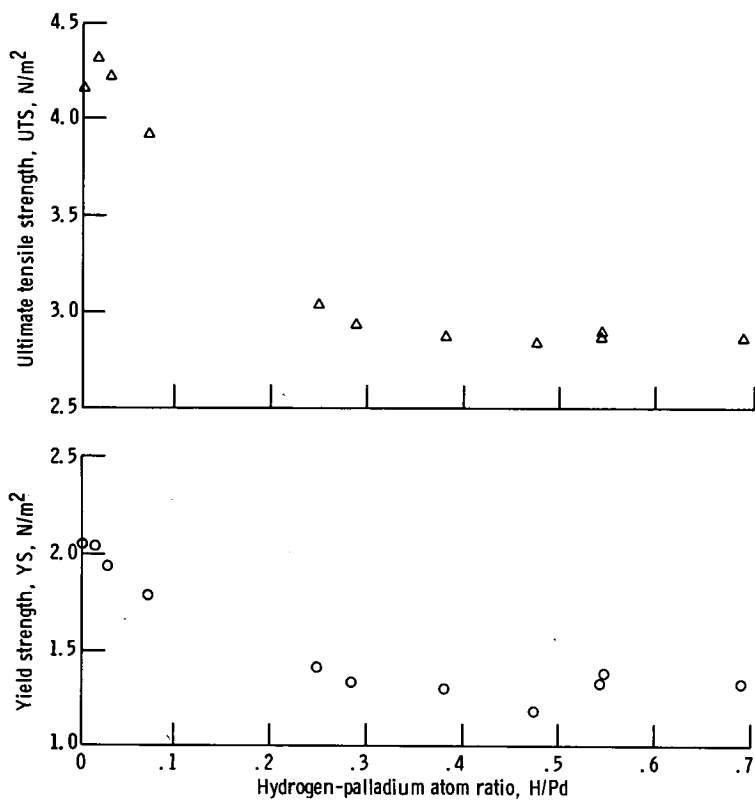
6) 90Pd-10Ag.

Figure 4. - Continued.

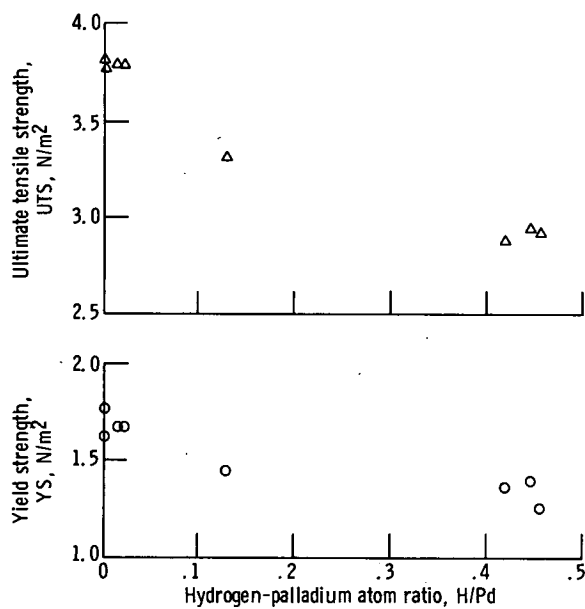


(c) 80Pd-20Ag.

Figure 4. - Continued.

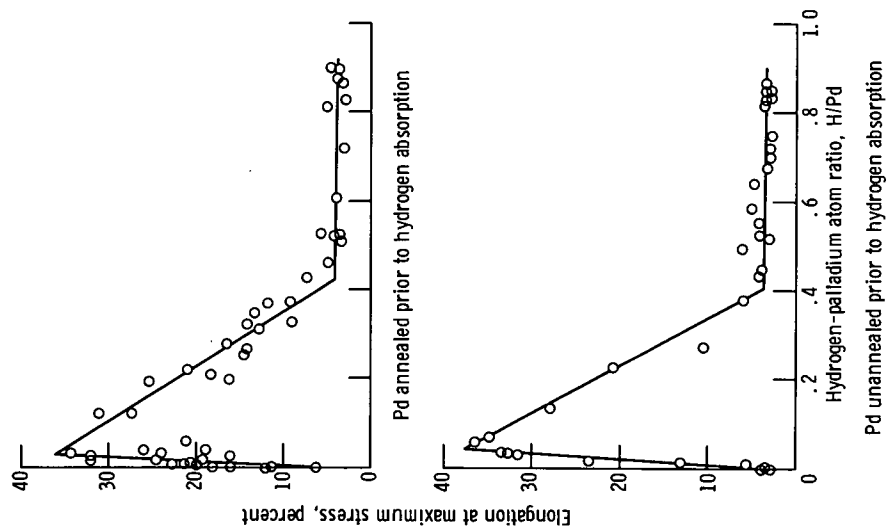


(d) 70Pd-30Ag.



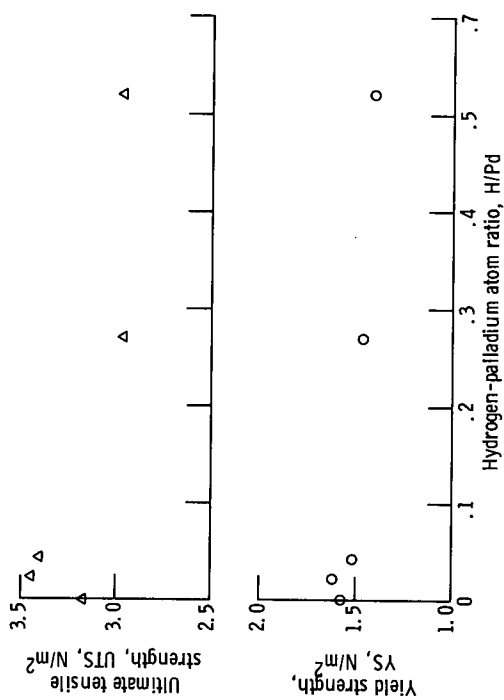
(e) 60Pd-40Ag.

Figure 4. - Continued.



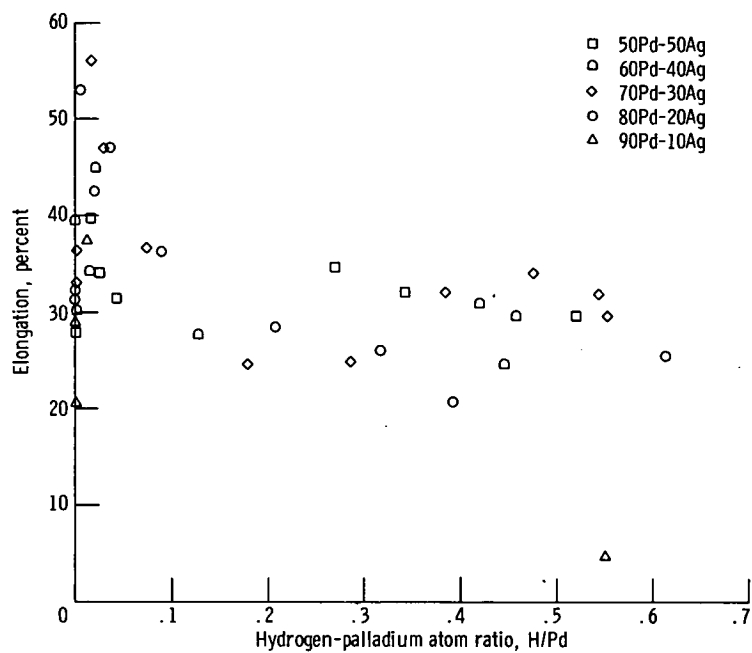
(a) Palladium.

Figure 5. - Percent elongation plotted against hydrogen content in palladium (Pd), 90Pd-10Ag, 80Pd-20Ag, 70Pd-30Ag, 60Pd-40Ag, and 50Pd-50Ag.



(f) 50Pd-50Ag.

Figure 4. - Concluded.



(b) 90Pd-10Ag, 80Pd-20Ag, 70Pd-30Ag, 60Pd-40Ag, and 50Pd-50Ag.

Figure 5. - Concluded.

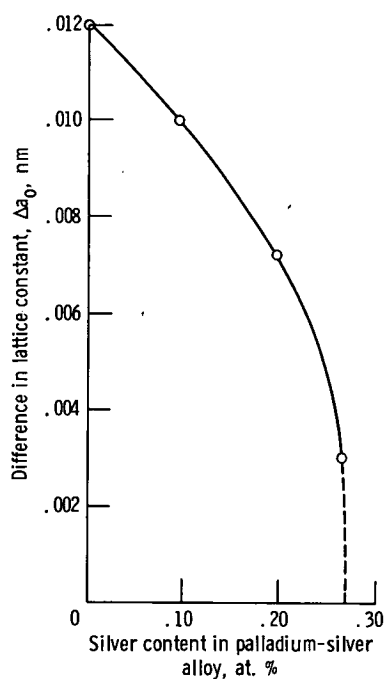


Figure 6. - Difference in lattice constant between α_{\max} and β_{\min} shown as function of silver in palladium for palladium-silver-hydrogen system.



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